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PATENT SPECIFICATION.

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COMPLETE SPECIFICATION.

An Improved Method of Making Tetra-Acetals of Glyoxal.

We, CARBIDE AND CARBON CHEMICALS CORPORATION, of 30, East, 42nd Street, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (Assignees of LOUIS GARDNER MACDOWELL and RAYMOND WILSON MCNAMEE, both Citizens of the United States of America, of R.F.D. No. 1, Box 403, Charleston, and 418, Forest Circle, South Charleston, respectively, State of West Virginia, United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

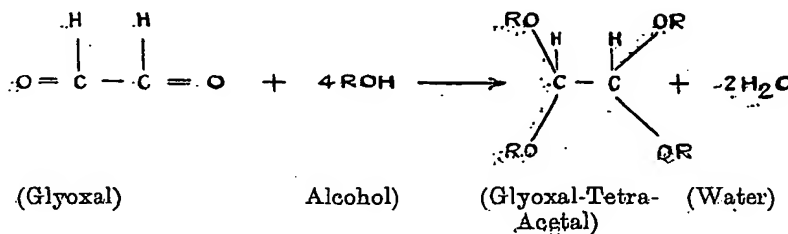
This invention relates to an improved method of making tetra-acetals of glyoxal.

It has been proposed to prepare glyoxal tetra-ethyl acetal by heating sodium ethoxide with the diethyl acetal of dichloroacetaldehyde. However, such process is not adapted for industrial use. It has also been proposed to prepare the same compound by heating trimeric

glyoxal with absolute ethyl alcohol in the presence of hydrochloric acid and permitting the reaction mixture to stand for a considerable period of time at room temperature. Recently, it has been proposed to prepare glyoxal tetra-acetals by the reaction of glyoxal sulphate with alcohols in the presence of a metal compound capable of forming an insoluble sulphate with the sulphuric acid formed during the reaction. However, all of these known processes are not adapted for commercial use due either to the long period of time required for carrying out the reaction or to the large amounts of acids and salts involved therein.

According to the process of the present invention, glyoxal tetra-acetals are readily obtainable in commercially acceptable yields by reacting glyoxal with an alcohol or with a glycol mono-ether, continuously removing water from the reaction mixture and recovering therefrom a glyoxal tetra-acetal.

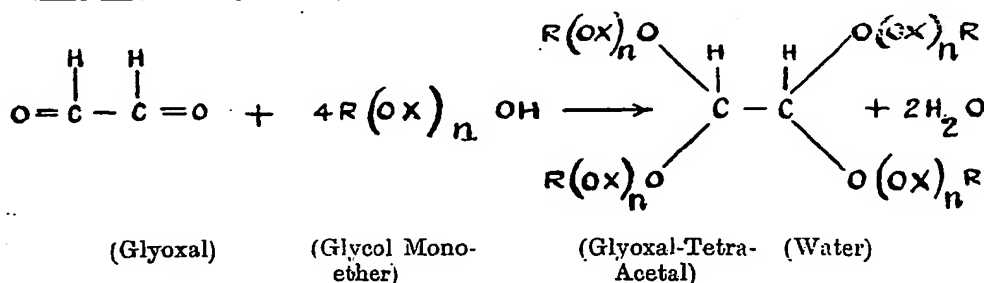
The reaction involved when an alcohol is employed as a starting material may be represented by the following scheme:



wherein R represents an alkyl or aralkyl. If a glycol mono-ether is employed as a starting material the reaction involved

may be represented by the following scheme:

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where X is an alkalene group having at least two carbon atoms, n is a small integer usually not exceeding about five or six, and R is an alkyl, aralkyl, or aryl group.

Both aromatic and aliphatic alcohols may be employed in this process, and good yields of the glyoxal tetra-acetals of the lower aliphatic alcohols, such as methyl, ethyl, isopropyl, beta-chlorethyl and butyl alcohols have been obtained. Good yields of glyoxal tetra-acetals have also been obtained by reacting the higher aliphatic alcohols (that is, those containing at least six carbon atoms), such as *n*-hexanol, 2-ethyl butanol, 2-ethyl hexanol, and the like with glyoxal. The latter mentioned glyoxal tetra-acetals are valuable as high-boiling solvents and as plasticizers, particularly for cellulose derivative and for polyvinyl acetal resins. In general, the glyoxal tetra-acetals prepared from the higher alcohols are insoluble in water and in the lower alcohols but they are soluble in many common organic solvents and in mineral oils. The glyoxal tetra-acetals prepared from the lower alcohols are powerful solvents of medium boiling points for oils, fats, resins and cellulose derivatives. Tetramethyl acetal is soluble in both water and in oils, and it forms a useful coupling agent in systems including such normally immiscible components.

The following monoglycol and polyglycol mono-ethers are representative of those suitable for use in making the new glyoxal tetra-acetals: the methyl, ethyl, propyl, isopropyl, butyl, 2-ethylbutyl, 2-ethylhexyl, benzyl, phenyl and toluyl mono-ethers of ethylene, propylene and butylene glycols and the corresponding mono-ethers of the di, tri, or tetra polyglycol modifications of these monoglycols.

The glyoxal tetra-acetals prepared by employing a mono-ether of a mono or polyglycol as a starting material are unique in that they contain a very high proportion of oxygen atoms bound in ether linkages. As a consequence they are extremely powerful solvents for oils,

fats, resins and cellulose derivatives. They serve admirably in processes for the extraction of essential oils, as well as alkaloids, and in processes for the removal of wax from hydrocarbons. Lower alkoxyalkyl tetra-acetals of glyoxal, such as glyoxal tetra (methoxy-ethyl) acetal are soluble both in water and in most classes of organic liquids, and they may act as a strong mutual solvent or coupling agent to bring into solution mutually immiscible liquids or to improve the stability of an emulsion of one such liquid in another. The higher alkoxy-alkyl tetra-acetals of glyoxal are insoluble in water and they are excellent plasticizers for cellulose derivatives, for polyvinyl acetal resins, and for casein. Some of the aromatic derivatives have mild fragrant odors and are useful in perfumery.

The method of making glyoxal tetra-acetals, according to this invention, involves heating glyoxal and an alcohol or a glycol mono-ether, preferably in the presence of a small amount of an acidic catalyst, and continuously removing the water of reaction as it is formed. Suitable acidic catalysts include mineral acids, such as hydrochloric and sulphuric acids, as well as mineral acid salts, such as aluminium sulphate or boron trifluoride. Because of the difficulty in handling and storing monomeric glyoxal, the glyoxal preferably is added in aqueous solution where it exists either in the form of a hydrate or a hydrated polymer, possibly tetrahydroxydioxane. In the present invention as described herein and defined in the appended claims, the designation "glyoxal" is intended to include monomeric glyoxal, as well as aqueous solutions of glyoxal, its hydrates, polymers, and hydrated polymers.

The amount of alcohol or glycol mono-ether employed is preferably more than that stoichiometrically required. It is essential to remove the water of reaction as the reaction progresses. If the alcohol or glycol mono-ether is water-immiscible

this continuous removal of water may be effected by distilling off a constant boiling mixture of water and alcohol, condensing such mixture and returning the alcohol or glycol mono-ether layer to the reaction vessel. Carrying out the process under reduced pressure will also facilitate removal of the water, especially when the acetal formed is that of a high boiling alcohol or glycol mono-ether. If the glyoxal is initially associated with water, such water will be removed along with the water formed in the reaction. Even when the large amounts of water are initially present, which may occur when an impure product containing a hydrated polymer of glyoxal is employed, yields of the tetra-acetal as great as 80% to 90% may be obtained.

Irrespective of the solubility in water of the alcohol or of the mono-glycol ether involved, the process may be carried out advantageously in the presence of a volatile, inert, water-immiscible liquid, such as benzene, toluene, xylene, hexane, ethylene dichloride, or isopropyl ether, and the water of reaction can be removed as an azeotropic distillate with this liquid. The temperature at which the process is conducted may vary from but slightly above atmospheric up to temperatures near the boiling point of the acetal products formed.

In the following examples, examples 1 to 4 inclusive illustrate the formation of glyoxal tetra-acetals employing an alcohol as a starting material while examples 5 and 6 illustrate the use of a glycol mono-ether as a starting material:

EXAMPLE 1:

Thirty-six and two-tenths (36.2) grams of an 80% aqueous glyoxal solution (containing 0.5 mol of glyoxal), 520 grams (4 mols.) of 2-ethyl hexanol, and 0.6 cc. of concentrated sulfuric acid were heated under reduced pressure in a vessel having a distillation column. An azeotropic mixture of water and 2-ethyl hexanol was continuously distilled from the vessel, condensed, and collected in a decanter where the water was separated from the remainder of the distillate, and from which the 2-ethyl hexanol was returned to the reaction vessel. After about 26 grams of water had been evolved, the excess 2-ethyl hexanol was removed by straight distillation. The residual liquid was washed with sodium bicarbonate solution to neutralize the catalyst and then distilled *in vacuo*. A 71% yield of the tetra (2-ethyl-hexyl) acetal of glyoxal was obtained. The major portion of this material boiled at 215°-235° C. at 2 to 3 mm. and possessed a specific gravity of 0.882 at 20° C. The material was

insoluble in water, methanol and ethanol, but it was soluble in many common organic solvents and in mineral oil.

EXAMPLE 2:

Fourteen hundred and fifty (1450) grams of impure aqueous glyoxal (containing 21.3% glyoxal) were placed in a distilling kettle with 2564 grams of butanol and 2 cc. of concentrated sulfuric acid. Distillation was started, and an azeotropic mixture of water and butanol was removed continuously. The distillate was condensed, the water decanted, and the butanol layer of the distillate returned to the kettle. When no more water could be distilled, 10 grams of sodium acetate were added to the reaction mixture to neutralize the catalyst and the excess butanol removed by distillation. Glyoxal tetra-butyl acetal was obtained in a yield of 85.8% based on the glyoxal charged. Glyoxal tetra-butyl acetal boils at 162° C. at 10 mm., and has a specific gravity of 0.890 at 20° C.

EXAMPLE 3:

Two hundred and fifteen (215) grams of an 81% aqueous solution of glyoxal, 1930 grams of ethylene chlorohydrin, 250 cc. of benzene and 0.5 cc. of concentrated sulfuric acid were heated together in a distilling vessel. A constant boiling mixture of water and benzene was distilled over, condensed, and collected in a decanter from which the water layer was removed and the benzene layer returned to the still column as a reflux. After 144 grams of water had been removed, two grams of potassium acetate were added to the reaction mixture and the excess of benzene was distilled off. A 45% yield of the tetra-(β -chloroethyl) acetal of glyoxal was obtained. This material is representative of a new class of chlorinated ethers and it boils at 187° to 188° C. at 4 to 5 mm., and has a specific gravity of 1.332 at 20° C. This chlorinated glyoxal acetal possesses merit as an addition agent for extreme pressure lubricants and it is useful in making rubber-like products by condensation with poly-sulfide compounds. In addition, its plurality of chlorine atoms make it a valuable intermediate for the synthesis of many compounds of unusual structure and properties. The chlorinated glyoxal tetra-acetals derived from other lower chlor-alkanols, such as propylene chlorohydrin and chlorbutanol, have similar properties and they may be prepared in like manner.

EXAMPLE 4.

Eleven hundred and ninety-five (1195) grams of a 48.5% aqueous solution of glyoxal (containing 10 mols of glyoxal), 3200 grams of methanol (100 mols) and 2 180

cc. of concentrated sulfuric acid were placed in a flask and rapidly distilled without reflux. The vapors were conducted into another flask which was equipped with an efficient fractionating column. The methanol which was obtained at the head of this column was returned continuously to the original reaction flask. After a period of time, the reaction mixture was distilled and a 38% yield of glyoxal tetramethyl acetal was obtained. This material boiled at 78° to 79° C. at 50 mm. and possessed a specific gravity of 1.018 at 20° C.

EXAMPLE 5.

Four hundred and fifty-five (455) grams of a 51% aqueous glyoxal solution (containing 4 mols of glyoxal), 2432 grams (34 mols) of the methyl ether of ethylene glycol, and 3 cc. of concentrated sulfuric acid were heated in a distillation kettle. The water evolved in the reaction, as well as that initially present, was removed continuously by straight distillation. At the completion of the reaction, that is, when all the water had distilled over, sodium acetate was added to neutralize the catalyst and the excess glycol ether was removed by straight distillation. A 63.4% yield of the tetra (methoxy-ethyl) acetal of glyoxal was obtained. This material boils at 183° to 185° C. at 5 mm. and possesses the specific gravity of 1.068 at 20° C. It is completely miscible with water and all common organic solvents.

EXAMPLE 6.

Thirty-six and two-tenths (36.2) grams of an 80% aqueous glyoxal solution (containing 0.5 mol of glyoxal), 472 grams of the monobutyl ether of ethylene glycol (4 mols), 0.6 cc. of concentrated sulfuric acid, and 200 cc. of toluene were heated together in a distillation kettle. A constant boiling mixture of water and toluene was distilled over, condensed, and collected in a decanter from which the water layer was removed and the toluene layer returned to the still column as reflux. After about 24 grams of water had been removed, the excess of toluene was distilled off. An 86.2% yield of glyoxal tetra (butoxy-ethyl) acetal was obtained. The major portion of this material boiled at 240° to 250° C. at 4 mm. and possessed a specific gravity of 0.961 at 20° C. It was insoluble in water, sparingly soluble in methanol and completely soluble in all other common organic solvents and in mineral oil.

Under hydrolyzing conditions, usually in the presence of acids, the glycol tetraacetals are slowly converted to glyoxal, and they constitute a source from which this highly reactive material may be

liberated. Thus, they can be used to render casein and other albuminous materials insoluble in water by reaction with glyoxal liberated from them. Likewise, they may also serve as the source of glyoxal in the reduction of vat and indigo dye-stuffs.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. A process of making a glyoxal tetraacetal which comprises reacting glyoxal with an alcohol or a glycol mono-ether, if desired, in the presence of an acidic catalyst, removing water continuously from the reaction mixture, and recovering therefrom a glyoxal tetraacetal.

2. A process as claimed in claim 1, which comprises employing a water-immiscible alcohol, distilling a mixture of water and alcohol from the reaction mixture, separating the alcohol from the water, and returning said alcohol to the reaction mixture.

3. A process as claimed in any of the preceding claims which comprises heating glyoxal with an alcohol or a glycol mono-ether in the presence of an inert, volatile water-immiscible liquid, and distilling a mixture of water and said liquid from such reaction mixture.

4. A process as claimed in claim 3, in which the water formed in the reaction is removed as a constant boiling mixture with said inert liquid.

5. A process as claimed in claim 4, in which an excess of an alcohol or glycol mono-ether is employed over that theoretically necessary to react with the glyoxal.

6. A process as claimed in any of the preceding claims in which the alcohol employed is a lower aliphatic alcohol, such as methyl, ethyl or isopropyl alcohol.

7. A process as claimed in claim 6, in which the lower aliphatic alcohol is a lower chloralkanol, such as beta-chloroethyl alcohol.

8. A process as claimed in claims 1 to 5, in which the alcohol employed is a higher aliphatic alcohol, such as *n*-hexanol, 2-ethyl butanol, or 2-ethyl hexanol.

9. A process as claimed in claims 1, 3, 4 and 5, in which the glycol mono-ether employed is a mono or polyglycol mono-alkyl or aryl ether.

10. A process as claimed in claim 9, in which the glycol mono-ether employed is the methyl, ethyl, propyl, isopropyl, butyl, 2-ethylbutyl, 2-ethylhexyl, benzyl, phenyl or toluyl mono-ether of ethylene, propylene and butylene glycols or is the corresponding mono-ether of the

corresponding di-, tri-, or tetra polyole-
fine glycols.

11. A process of making a glyoxal
tetra-acetal by reacting glyoxal with an
5 alcohol or a glycol mono-ether as herein-
before particularly described.

12. Glyoxal tetra-acetals whenever ob-

tained by the process hereinbefore par-
ticularly described.

Dated this 16th day of February, 1942.

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